

XAFS STUDY OF SULFUR FORMS IN COALS DURING RAPID PYROLYSIS

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ABSTRACT

Various kinds of coal, having the same average diameter and 89% C daf, were pyrolyzed rapidly in a free-fall reactor at atmospheric pressure under a nitrogen stream at a terminal temperature of 1253 K. The extent of organic sulfur removal in the rapid pyrolysis were different. Sulfur K-edge X-ray absorption near edge structure indicated that the organic sulfur species removed from coals were elemental, disulfide, sulfide and sulfoxide sulfur. The extent of organic sulfur removal in the rapid pyrolysis depended on the coals, because the amount and fraction of the volatile organic sulfur species were different even when the coals have the same carbon content.

1. INTRODUCTION

Sulfur is one of the most troublesome contaminants in coal. Although, present only in low concentrations, sulfur causes problems in every process that uses coal. When released into the atmosphere as SO₂ through combustion, it produces so-called acid rain. Certainly, a better understanding of the nature and distribution of sulfur-bearing minerals, organic sulfur-containing functional groups and their concomitant chemistry is necessary for improving advanced coal preparation processes and the environmental acceptability of coal-derived energy. Sulfur takes on several forms in coal including elemental, mineral and organic. Conventional coal cleaning technologies are grouped into physical and chemical methods. Because physical processes are limited to removal of inorganic constituents, development of an efficient process of organic sulfur removal is an urgent issue for sustainable resource development and environmental conservation. Development of a chemical desulfurization process requires a detailed understanding of organic sulfur forms in coal.¹ X-ray absorption near edge structure (XANES) spectroscopy has been shown to be a powerful method for the direct, nondestructive, and quantitative determination of organic sulfur-containing functional groups forms in coal.²⁻⁴

In the present study, dynamic behaviors of sulfur forms for several coals were followed in rapid pyrolysis. These coals were first served as a lumped sample which had the same average particle diameter without density separation. Then, the same samples were separated into three groups by a sink-float method to investigate effects of particle-density distribution on sulfur forms and their desulfurization behavior in rapid pyrolysis. Organic sulfur forms were determined by using XANES for the density-separated coals before and after pyrolysis.

2. EXPERIMENTAL

The coal samples were used in the experiment as soon as received. Average particle size of the sample was 0.35 mm. The samples were separated into three density groups by a sink-float method in zinc chloride aqueous solution. The absence of zinc chloride in the density-separated sample was confirmed by extraction with 5 M HCl for 2 h.

Rapid pyrolysis experiment was conducted by using a free-fall pyrolyzer. This apparatus enables coal particles to be heated in a nitrogen stream at rates from 10³ to 10⁴ K/s depending on particle density and diameter. Particle residence time is varied by changing the length of the heating section. The temperature was 1253 K at the isothermal section of the reactor.

Sulfur K-edge X-ray absorption near edge structure spectroscopy was applied to specifying the forms of organic sulfur in raw and char. XANES measurements were carried out at beam line 2A of Photon Factory in the National Laboratory for High Energy Physics. Si(111) monochromator was used to vary the incident X-ray energy. The beam irradiated the samples fixed on a nickel plate under 10⁻³ Pa in a vacuum chamber. Data were recorded in the fluorescence and electron yield modes in the region of the S K-edge at room temperature. The absolute photon energy was calibrated with the

assumption that the giant resonance of K_2SO_4 ($S\ 1s \rightarrow t_2$) appears at 2481.7 eV. The third derivatives of XANES spectra from model compounds were used as fingerprints for interpreting sulfur forms in the sample. Ferrous sulfide, pyrite, crystalline sulfur, DL-cysteine, thioxane-9-one, S-methyl-L-cysteine, DL-methionine sulfoxide, and potassium sulfate were selected as the model compounds.

3. RESULTS AND DISCUSSION

Table 1 shows proximate, ultimate, and sulfur-form analyses for the sample coals. Figure 1 shows a correlation between extent of organic sulfur removal and carbon content for Nantong, Yanzhou, and Furong coals being studied in the present work, and for other 13 coals, carbon content ranging from 65 to 90% daf. The extent of organic sulfur removal is defined by

$$\{1 - (\text{organic sulfur in char}) / (\text{organic sulfur in raw coal})\} \times 100 (\%)$$

where ultimate content of organic sulfur in the rapid pyrolyzed char based on coal basis was used as organic sulfur in char in this equation. By considering the thermal stability of thiophenic, and sulfide sulfur, it is plausible that the extent of organic sulfur removal decreases linearly with the increase of carbon content due to the increase of thiophenic sulfur content.

Table 1. Analyses of Sample Coals

sample	ultimate (wt %, daf)					proximate (wt %, db)		sulfur form (wt % of total sulfur)		
	C	H	N	S	diff	VM	ash	pyritic	sulfate	organic
Nantong	88.9	4.9	0.6	5.0	0.6	17.0	17.3	34	1	65
Yanzhou	89.1	5.5	1.1	3.2	1.1	43.2	9.1	38	1	61
Furong	88.9	3.1	0.9	6.6	0.5	10.5	21.6	77	0	23

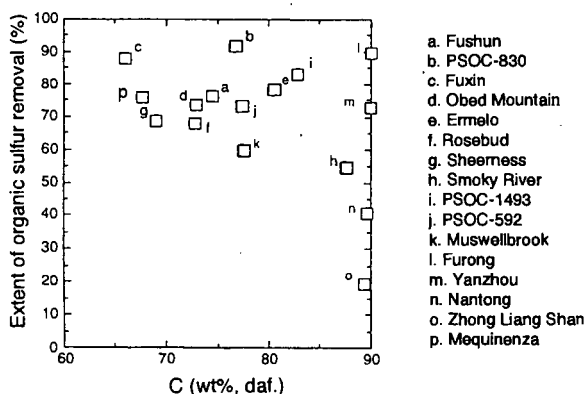


Figure 1. Change in extent of organic sulfur removal from solid phase with carbon content.

An apparent linear correlation, however, cannot be obtained between the extent of organic sulfur removal in rapid pyrolysis and carbon content of raw coals as demonstrated in Figure 1. The large difference from 19% to 89% of the extent of organic sulfur removal was noted for five kinds of high-rank coals containing more than 87% carbon. High-rank Furong coal was desulfurized to 89%, the second highest extent of desulfurization in 16 coals.

Figure 2 shows a relation between yield and density obtained by the sink-float method in zinc chloride aqueous solution. The density distribution differs from coal to coal even through carbon content is the same. The samples were separated into three groups with expected differential concentration of macerals.⁵ The range of each group was altered in three kinds of coal to obtain enough amount of fractionated samples to be supplied for rapid pyrolysis experiments.

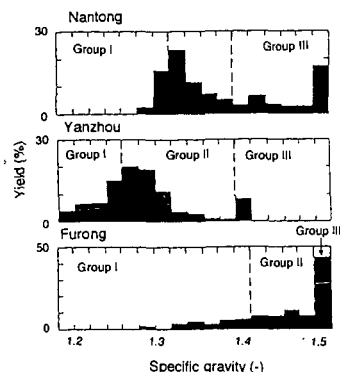


Figure 2. Yield distribution in density separation.

The raw and separated samples, group I, II, and III, were rapid pyrolyzed in a nitrogen stream with the free-fall reactor. Figure 3 represents a relation between the extent of organic sulfur removal and average density. Nantong and Yanzhou coals show linear relationship between the extent of organic sulfur removal and average density of the groups in each coal. This result implies that thermally stable organic sulfur increases with the increase on density. The existence of thermally stable organic sulfur is expected in the group III of Nantong and group II of Furong coals because of smaller extent of organic sulfur removal than volatile yield. Group I of Furong coal showed larger extent of organic sulfur removal than group II as the same tendency as the other coals though volatile yield was independent of average density. Exceptionally, more than 90% of the extent of organic sulfur removal was observed for group III of Furong coal, although the low extent of organic sulfur removal was expected because of high rank coal.

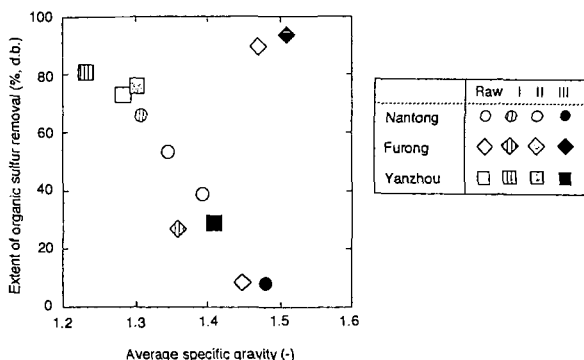


Figure 3. Change in organic sulfur removal with average density.

Figure 4 shows third differential curves of XANES spectra for groups I and III of Nantong coal. Strong peak is observed around 2472 eV for group I, which are attributable to thiophene and sulfide. A strong peak at 2474.5 eV results from sulfoxide. Through group III shows the similar distinct peaks of thiophene and sulfoxide to group I, the sulfide peak dose not appear for group III. It could be estimated that efficient desulfurization in a smaller density group such as group I is related to the presence of sulfide though the absolute amount of each sulfur form should be determined.

Third differential curves of XANES spectra for groups I and III of Furong coal are shown in Figure 5. Thiophene, sulfoxide, and pyritic sulfur are observed for group I as the same as the curves of Nantong, group I. On the other hand, the curves for group III of Furong are very different from that of group I. In addition to the peaks resulting from thiophene, sulfoxide, and sulfate, intensive peaks are observed at 2470.4-2470.8 eV, which are combined peaks attributable to pyritic sulfur and elemental sulfur. Figure 6 represents third differential curves of XANES spectra of rapid pyrolysis chars for group I and III of Furong coal. The curve of char for group I indicates that the sulfoxide peak becomes

smaller after pyrolysis while the peak of thiophenic sulfur remained. A peak at 2468.7 eV resulted from ferrous sulfide produced by reduction of pyrite. The peaks of pyritic sulfur and elemental sulfur disappeared and a large peak of ferrous sulfide at 2468.7 eV newly appeared after pyrolysis for group III. Furong coal has distinguishing characteristics as high organic sulfur content and removal extent of organic sulfur in larger density group III. XANES analysis, however, indicated that efficient extent of organic sulfur removal might be caused by releasing of elemental sulfur rather than organic sulfur.

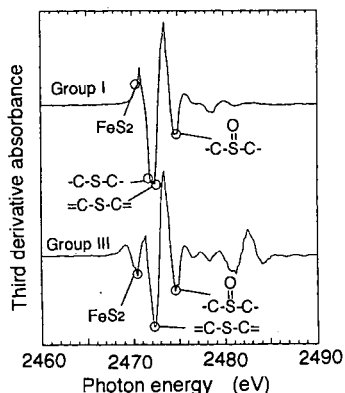


Figure 4. Sulfur K-edge XANES spectra of group I and III for Nantong coal.

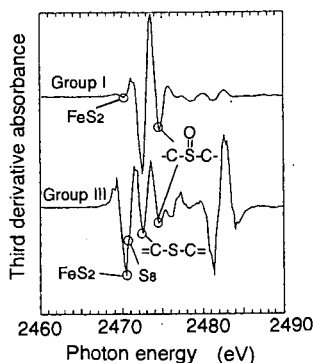


Figure 5. Sulfur K-edge XANES spectra of group I and III for Furong coal.

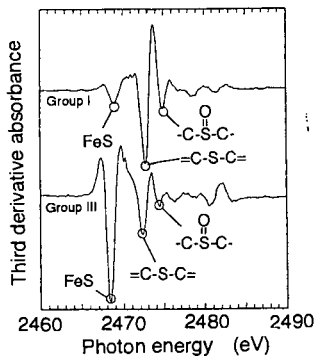


Figure 6. Sulfur K-edge XANES spectra of char for Furong coal.

4. Conclusion

In a serious on chemical coal cleaning, the desulfurization behavior in rapid pyrolysis was investigated for raw coals and their density-separated samples. The extent of organic sulfur removal shows linear decreasing tendency with the increase of density for each sample coal though the extent of organic sulfur removal was different from coal to coal even with the same carbon content. The high extent of desulfurization was estimated to be caused by elemental sulfur in the large density group of high-rank Furong coal.

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